

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 1 050 606 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:
08.11.2000 Bulletin 2000/45

(21) Application number: 97955055.5

(22) Date of filing: 17.12.1997

(51) Int. Cl.⁷: C25D 11/06

(86) International application number:
PCT/RU97/00408

(87) International publication number:
WO 99/31303 (24.06.1999 Gazette 1999/25)

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE

(71) Applicant: Isle Coat Limited
Douglas, Isle of Man, IM1 2PT (GB)

(72) Inventor:
SHATROV, Alexandr Sergeevich
Moscow, 119619 (RU)

(74) Representative:
Harrison Goddard Foote
Tower House,
Merrion Way
Leeds LS2 8PA (GB)

(54) **METHOD FOR PRODUCING HARD PROTECTION COATINGS ON ARTICLES MADE OF ALUMINIUM ALLOYS**

(57) The proposed invention relates to the sphere of plasma electrolytic oxide coating of aluminium alloys. The method incorporates anode-cathode oxide coating in an alkaline electrolyte at a temperature of 15-50°C, using 50-60 Hz frequency alternating current. In the initial stage of the process oxide coating is carried on for 5-90 seconds at a current density of 160-180 A/dm², then the current density is dropped to 3-30 A/dm² and the process is continued in a regimen of spontaneous diminution of power demand without on-line adjustment of the regimen until the set coating thickness is achieved. The alkaline electrolyte used is an aqueous solution of alkaline metal hydroxide at 1-5 g/l, an alkaline metal silicate at 2-15 g/l, an alkaline metal pyrophosphate at 2-20 g/l and peroxide compounds at 2-7 g/l (in terms of H₂O₂ - 30%). The proposed method enables the protective properties of ceramic oxide coatings to be enhanced through an increase in the micro-hardness, density and strength of adhesion to the substrate without any additional energy outlay or time required.

EP 1 050 606 A1

in anode voltage.

[0018] The hydroxide phases, however, possess rectifying properties. Consequently the imposition of pulses of negative polarity (anode-cathode process) causes breakdowns at places where the coating is unipolar in nature. The anode discharge following a cathode discharge begins at a high oxide layer permeability. Thus with alternating current polarisation of an aluminium alloy electrode, a dense oxide coating of even thickness is formed thereon.

[0019] The technical design proposed in the method for which the application is being made involves delivering heteropolar pulses to the electrode both at the initial stage of the process at a high current density, and also in an established regimen at an optimal current density, which is substantially different to the known methods.

[0020] The positive effect is obtained by the occurrence of powerful micro-arc discharges at the high current density values in the initial period of oxide coating which provide intensive mixing of the substrate metal and the oxide films. This increases the mutual diffusion of the substrate substance and the coating and helps to increase the strength of their adhesion. Analysis of the boundary between substrate and coating shows a blurred adhesion zone, indicating the formation of an enlarged diffusion zone. During such a short time interval the non-productive electric energy consumption is minimal, and the electrolyte temperature in the bath changes very little.

[0021] The time taken to attain the established sparking regimen, and consequently also the overall oxide coating time, are reduced by 10-25%.

[0022] The threshold current density and oxide coating process duration values have been verified experimentally. The current density in the initial stage of 160-180 A/dm² was determined from the condition of the maximum rate of oxide coating of aluminium with selected electrolyte composition. The duration of the initial stage is selected specifically for each alloy, but increasing the time above 90 seconds does not bring about any perceptible changes in the quality of the coating, though it does cause higher electricity consumption.

[0023] To obtain even oxide coatings, especially on items of complex shapes, at the established stage of the oxide coating process it helps to alternate an anode-cathode process with a cathode process, in which only cathode pulses are delivered to the item and there is additional activation of the surface being coated. In this case the power source is equipped with a unit for regimen cycling which sequentially switches in and out the anode-cathode or cathode regimen for set durations. The duration of delivery of anode-cathode pulses is 5-30 seconds, and the duration of delivery of cathode pulses is 1-10 seconds. The current density of the cathode pulses during the cathode regimen is 5-25% of the current density during the anode-cathode regimen. The alternation of anode-cathode and cathode regimens helps to produce denser and less porous coatings of even thickness.

[0024] Examples of the shape of the pulses of the process current and their sequence in time with the different electrolysis regimens are illustrated in graph form in Figures 1-4.

FIGURE 1 illustrates the current shape in an anode-cathode regimen, when the polarisation is obtained through an alternating sinusoidal current.

FIGURE 2 illustrates the current shape in an anode regimen when the polarisation is obtained solely through an anode current.

FIGURE 3 illustrates the current shape in a cathode regimen when the polarisation is obtained solely through a cathode current.

FIGURE 4 illustrates the current shape in an anode-cathode regimen with cathodisation, when an alternation (with set periods) is carried out between alternating current polarisation and purely cathodic amplitude-asymmetrical polarisation, where:

- A - current amplitude in anode-cathode period;
- a - current amplitude in cathode regimen (cathodisation);
- a = 0.05-0.25;
- T_{ac} - duration of anode-cathode period, T_{ac} = 5-30 s;
- T_c - duration of cathode period, T_c = 1-10 s.

[0025] Attempts to use peroxide compounds in electrolytes as a source of chemically-bonded oxygen have been made by several researchers (US, A. 5275713; US, A. 5069763; SU, A1. 1767094). The problems here have been in the instability of the solutions, since the intensity of breakdown of the peroxide compounds rises under the influence of alkalis, heat light and so on.

[0026] According to this invention, the addition of peroxide compounds to the composition of a known electrolyte gives the new composition new properties. The alkaline metal pyrophosphate (to a greater extent) and the alkaline metal silicate (to a lesser extent) that are present in the composition of the electrolyte are excellent hydrogen-peroxide-

based oxidant stabilisers.

[0027] Despite the fact that pyrophosphates give solutions with a higher pH than other phosphates, for example Na_2HPO_4 , the H_2O_2 stabilisation effect is much more strongly manifested in them. When prepared electrolyte is kept for 10 days, no breakdown of H_2O_2 occurs. This enables the new electrolyte composition to be utilised in industrial production.

[0028] The introduction of peroxide compounds into an alkaline pyrophosphate-silicate electrolyte has a positive impact both on the electrolysis process and on the quality of the coating formed.

[0029] Hydrogen peroxide is simultaneously a source of free OH radicals and of oxygen. Diffusion of oxygen moving out of the electrolyte towards the surface of the electrode with dissociation of H_2O_2 leads to intensification of thermochemical plasma reactions on the surface of the item being coated. The rate of oxide layer formation is increased by 10-25%. The micro-hardness of the coating is also increased through a rise in the aluminium oxide content in the phase composition of its high-temperature alpha phase.

[0030] The specific nature of the oxide coating process in the new electrolyte is, moreover, associated with an increased capture of free electrons in the solution by the peroxide anion and, consequently, with an increase in the energy of the positive ions coming into the solution from the discharge. The result of this effect is a more intensive polymerisation of pyrophosphate and silicate. Initiation of polymerisation and polycondensate chains in the solution leads to intensive formation of insulating layers on the electrode, which causes an increase in the breakdown voltage, and this in turn leads to a rise in the micro-hardness of the coating.

[0031] Finally, systems of various inorganic polymers and oxides of aluminium are formed with mutually penetrating and mutually reacting structures, which makes the coating elastic and resistant to vibration and impact loads.

[0032] The threshold values of component concentrations in the electrolyte composition are determined experimentally. At component concentrations below the threshold values indicated, the oxide coating process continues at high current densities, and the coatings that are obtained are uneven, with enhanced porosity around the edges of the item. A rise in the component concentration above the threshold values causes thick, brittle and inelastic coatings to be obtained.

[0033] Among the peroxide compounds which may be utilised are hydrogen peroxide and/or alkaline metal peroxides (Na_2O_2 , K_2O_2 , Li_2O_2), or alkaline metal peroxy-solvates (peroxyphosphate, peroxycarbonate, peroxyborate and so on).

[0034] The invention is illustrated by the example given below and in the table. A 200 mm diameter disc of D16 alloy (AlCu_4Mg_2), 20 mm deep, machined to the set size, was subjected to oxide coating (surface to be coated 7.5 dm^2). The item was immersed on a current supply into a 600 litre bath which was a counter-electrode, and a compressor was switched on to bubble air through the electrolyte. The electrolyte used was based on distilled water with 2 g/l caustic potash, 3 g/l sodium silicate glass, 4 g/l sodium pyrophosphate and 3 g/l hydrogen peroxide (30%). With the aid of a 125 kW power source, positive and negative voltage pulses (anode-cathode regimen) were delivered in an alternating sequence to the item and the bath at 50 Hz frequency. During the first 10 seconds, oxide coating was carried on at a current density of 160 A/dm^2 , then the current density was lowered to 10 A/dm^2 and oxide coating was continued without any further interference until a coating thickness of 130 microns was achieved. The current density at the end of the process was 6 A/dm^2 . The electrolyte temperature was maintained in the $35\text{-}45^\circ\text{C}$ range. After oxide coating, the items were washed in warm water and dried at 80°C .

[0035] In the oxide coating process, the average current in the circuit and the amplitude values of the anode and cathode components of the power voltage were monitored. The instantaneous current and voltage values were recorded using an oscillograph. The strength of the adhesion between the oxide coating and the metal was determined using a pin method (calculated as the ratio of the detachment force to the area of damaged coating). The micro-hardness was measured on taper micro-sections (calculated as the arithmetic mean value after 10 measurements at different oxide layer depths).

[0036] The table gives a comparison of the electrolysis regimens and the coating characteristics obtained on items of AlCu_4Mg_2 alloy using the known methods and the proposed method.

[0037] As may be seen from the table, the proposed method provides the following technical and economic benefits: wear-resistant coatings of comparable thickness are formed 1.1-1.25 times more quickly without increasing the electricity consumption. At the same time the micro-hardness of the coating is increased by 15% on average, and the strength of adhesion to the substrate material rises by 15-20%.

[0038] The proposed method thus enables ceramic-oxide coatings with good protective and physical/mechanical properties to be obtained reliably on aluminium alloys. The coatings have a high micro-hardness and high strength of adhesion to the substrate metal, which virtually precludes delamination during use.

[0039] The electrolyte used in the proposed method features exceptional stability and presents no environmental hazard. It contains no chlorides, fluorides, ammonia or heavy metal salts.

[0040] The method is put into effect on simple and reliable process equipment using commercial frequency alternating current with minimal operating costs.

Commercial applicability

[0041] The proposed method may suitably be used to apply wear-resistant coatings to aluminium alloy items operating in environments where abrasive and corrosive factors are present, for example, pistons and cylinder liners of internal combustion engines, pump and compressor parts, hydraulic and pneumatic equipment parts, plain bearings, stop and control valves, radiators, heat exchangers, etc.

Table

Electrolyte composition, electrolysis regimens, coating and oxide coating process characteristics	Known method (DE 4209733)	Known method (RU 2070622)	Proposed method
1. Electrolyte composition: Potassium hydroxide, g/l Sodium silicate, g/l Sodium pyrophosphate, g/l Hydrogen peroxide, (30%) ml/l Distilled water, l	2 9 - - <1	1 2 3 - <1	2 3 4 3 <1
2. Coating formation regimens: Anode voltage amplitude at end of process, V Cathode voltage amplitude at end of process, V Current density (anode and cathode), A/dm ² -in initial stage - in established stage Electrolyte temperature, °C Oxide coating time, min.	690 300 - 6 30 180	720 350 - 8 40 150	780 320 160 10.6 40 135
3. Coating characteristics: Oxide coating thickness, microns Micro-hardness, Gpa Strength of adhesion to substrate, Mpa	100 16.0 297	130 16.4 309	130 18.6 358

Table (continued)

Electrolyte composition, electrolysis regimens, coating and oxide coating process characteristics	Known method (DE 4209733)	Known method (RU 2070622)	Proposed method
4. Process characteristics: Per unit energy demand, kWh.dm ⁻² /micron Electrolyte stability, A.h/l	0.090 30-90	0.085 180-400	0.080 150-300

15 Claims

1. A method of obtaining protective coatings on aluminium alloy items, the method including an anode-cathode oxide coating process in an alkaline electrolyte at a temperature of 15-50°C, using 50-60 Hz alternating current characterised in that in an initial stage of the process, oxide coating is carried out for 5-90 seconds at a current density of 160-180 A/dm², the current density is then reduced to 3-30 A/dm² and the process is continued in a regimen of progressively diminishing power demand until a coating of a required thickness is obtained.
2. A method according to claim 1, wherein oxide coating in a diminishing power demand regimen is carried out with alternation of anode-cathode and cathode regimens, a duration of delivery of anode-cathode pulses being 5-30 seconds and a duration of delivery of cathode pulses being 1-10 seconds, and wherein a current density of the cathode pulses in the cathode regimen is 5-25% of a current density of the anode and cathode pulses in the anode-cathode regimen.
3. A method according to claim 1 or 2, wherein the electrolyte is an aqueous solution of alkaline metal hydroxide at 1-5 g/l, an alkaline metal silicate at 2-15 g/l, an alkaline metal pyrophosphate at 2-20 g/l and peroxide compounds at 2-7 g/l (in terms of H₂O₂ - 30%).
4. A method according to claim 3, wherein the peroxide compounds are hydrogen peroxide and/or alkaline metal peroxides or alkaline metal peroxo-solvates.

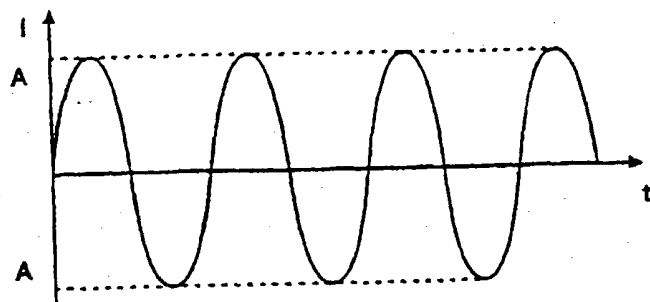


FIG. 1

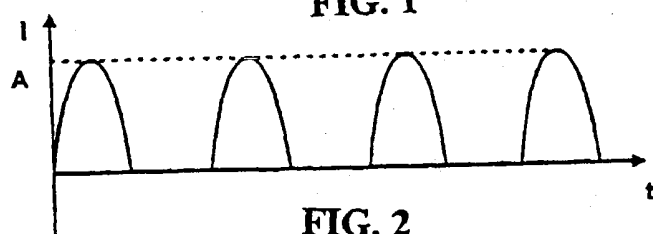


FIG. 2

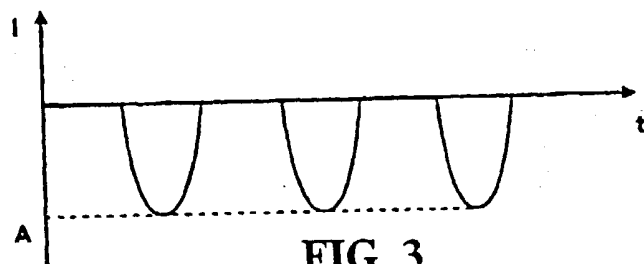


FIG. 3

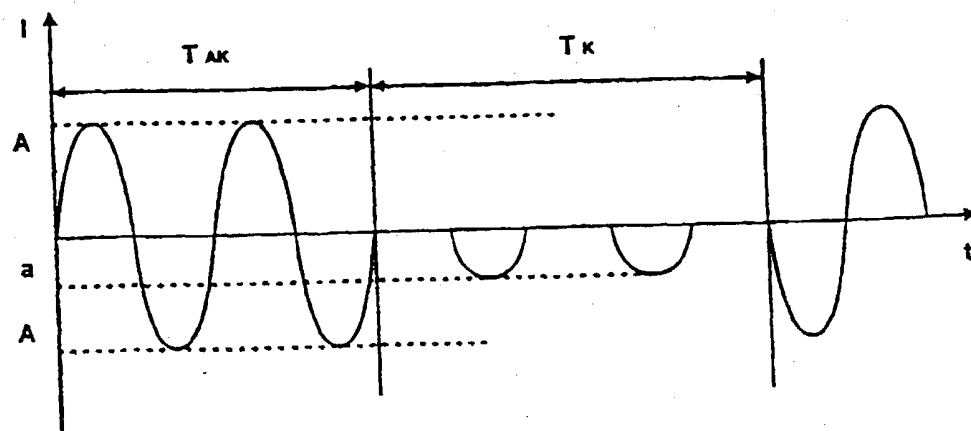


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 98/00408A. CLASSIFICATION OF SUBJECT MATTER⁶:

IPC6: C25D 11/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C25D 9/06, 9/12, 11/00, 11/02, 11/04, 11/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	RU 2070622 C1 (BOISHAKOV Vasily Alexandrovich et al.) 20 December 1996 (20.12.96).	1-3
A	US 5275713 A (RUDOLF HRADCOVSKY) 4 January 1999 (04.01.94).	1,4
A	WO 95/18250 A1 (NAUCHNO-ISSLEDOVATELSKY INZHENERNY TSENTR "TORIS") 6 July 1995 (06.07.95).	1-2
A	RU 2070947 C1 (MALYSHEV Vladimir Nikolaevich) 27 December 1996 (27.12.96).	1-2
A	RU 94023296 A1 (TJUMENSKY INDUSTRIALNY INSTITUT) 10 April 1996 (10.04.96).	1
A	SU 1713990 A2 (INSTITUT NEORGANICHESKOI KHIMII SO AN SSSR) 23 February 1992 (23.02.92).	1
A	SU 1200591 A (INSTITUT NEORGANICHESKOI KHIMII SO AN SSSR) 7 April 1989 (07.04.89).	1



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
4 August 1998 (04.08.98)Date of mailing of the international search report
26 August 1998 (26.08.98)

Name and mailing address of the ISA/

Authorized officer

Facsimile No. RU

Telephone No.